

8 Dispersion Forces

8.1 The Work of Adhesion and Cohesion and Dispersion Forces

8.1.1 The Work of Adhesion and Cohesion

The term, soap, is applied to the sodium or potassium salts of long-chain fatty acid. In general, these are examples of amphiphilic or amphipathic molecules which consist of two well-defined parts: one which is oil-soluble (lyophilic, oleophilic, or hydrophobic) and another which is water-soluble (hydrophilic). The hydrophobic part is non-polar and usually consists of aliphatic or aromatic hydrocarbons. The hydrophilic part consisting of halogen groups is polar and interact strongly with water.

The hydrophilic or hydrophobic properties are related with the work of adhesion and cohesion. The work of adhesion per unit area is defined by the work done on the system when two condensed phases (1 and 2), forming an interface of unit area, are separated in vacuum reversibly to form unit areas of each of the 1 and 2 surfaces.

$$W_{12}^{\text{adh}} = \gamma_1 + \gamma_2 - \gamma_{12} \quad (8.1)$$

where γ 's are surface tensions. The work of adhesion is the Helmholtz free energy of separation. The work of cohesion, on the other hand, is the work of adhesion when a substance, 1, is separated into two by creating two free surfaces of the same substance, 1, in vacuum.

$$W_{11}^{\text{coh}} = 2\gamma_1 \quad (8.2)$$

Note that since all substances are attracted each other in vacuum W^{adh} and W^{coh} are positive.

8.1.2 van der Waals' Forces

The intermolecular forces are responsible for the surface tension. The important interaction energies among nonpolar electrically neutral particles are van der Waals' or dispersion energies, which are attractive and pairwise additive. Quantum-mechanics gives an expression, $-\beta_{12}/r_{12}^6$, for the attractive energy between two molecules, 1 and 2, where β_{12} is a constant and r_{12} is the distance between the two molecules. (The center of the molecules is suitably defined in determining r_{12} .) Consider two particles, 1 and 2, separated at a certain distance. Suppose that the particle 1 contains many molecules with the number density ρ_1 and the particle 2 does with ρ_2 . Then, the contribution of the attractive energies to the Gibbs free energy at $T=0$ is given by

$$\Delta G_{12}^d = - \int_{v_1} dv_1 \int_{v_2} dv_2 \frac{\beta_{12} \rho_1 \rho_2}{r_{12}^6} \quad (8.3)$$

where v_1 and v_2 are the volume of the particles, 1 and 2, respectively. It is usually assumed that the number densities are constant at least within the respective particles. Hence,

$$\pi^2 \beta_{12} \rho_1 \rho_2 \equiv A_{12} \quad (8.4)$$

is a constant, called the Hamaker constant. This constant can be taken out of the integral, so that Eq. 8.3 is reduced to the integral which depends only on the geometry of the system.

It is important to realize that the Hamaker constant is independent of the geometry of the system, but the interaction energy depends also on the geometry. Hamaker (1937) used Eq. 8.3 for two spheres and Mahanty and Ninham (1976) applied Eq. 8.3 to various geometries (Exercise 8.1). However, we note that the Hamaker constant may depend on the particle size ($< \sim 10$ nm) due to a quantum effect (see Sec. 1.2).

Verwey and Overbeek (1948) experimentally found that, when two particles are separated by distances large compared to a certain value (λ_0), the observed energy is considerably less than the prediction of Eq. 8.3. The value λ_0 corresponds to the wavelength defined by the ionization potential ($\hbar\omega_0$ =the ionization potential energy) of the molecules. Classically, we may consider that the attractive dispersion energy, $-\beta_{12}/r_{12}^6$, between two molecules, 1 and 2, occurs because of the oscillating electric dipole moments of orbiting electrons around their respective nuclei. The oscillating moment in molecule 1 polarizes the molecule, 2, and vice versa. The induced dipole moment, say, in molecule 2 in turn generates an oscillating electric field back at molecule 1, which interacts with the dipole moment of molecule 1. The interaction energy depends on the phases of the oscillating field and the dipole moment. Verwey and Overbeek postulated that the interaction energies decrease with distances because the time of electric field propagation from

Table 8.1 Surface tension (energy) and the dispersion contribution

	γ erg/cm ²	γ^d	γ^{polar}
n-hexane	18.4	18.4	0
n-heptane	20.3	20.3	0
n-octane	21.3	21.3	0
n-nonane	22.7	22.7	0
n-decane	23.4	23.4	0
chloroform	27.2	25.9	1.3
dichloromethane	28.1	26.5	1.6
diethyl ether	17.1	15.0	2.1
tetrahydrofuran	26.7	22.5	4.2
ethyl acetate	23.8	19.6	4.2
acetone	23.3	16.5	6.8
water	72.8	21.8	51.0

molecule 1 to molecule 2 and back, 2 to 1, is such that the fluctuating electric field returns back to the originating dipole moment slightly out of phase. Casimir and Polder (1948) showed that a correction factor is necessary, called “retardation”, because of the finite speed c of light. The retardation expression (Clayfield et al. 1971) is complicated but an empirical representation of the correction factor is given by Overbeek (1952):

$$F(p) = 1.10 - 0.14p \quad \text{for } p < 3$$

$$2.45/p - 2.04/p^2 \quad \text{for } 3 < p \quad (8.5)$$

where $p = 2\pi r/\lambda_0$ and $\lambda_0 = c/(\text{ionization potential}/\text{Planck's constant})$. Since the fluctuating fields are responsible for the retardation, the electrostatic theory cannot treat the retardation.

The surface tensions in Eqs. 8.1 and 8.2 are caused not only by intermolecular dispersion forces but also due to molecular polar structures, chemical bondings, etc. (see Table 8.1). For instance, the dispersion contribution to the surface tension of water is only 30% of the total surface tension. The rest arises from the permanent dipole moment and H-bonding. On the other hand, the surface tension of hydrocarbons solely comes from the dispersion forces.

Recently, the contribution of the polar part of molecules to the surface tension has been considered to be rather small in solutions or at interfaces, although the contribution from the polar part is important in molecular interactions in the gaseous state. The polar interactions in water vapor are important, being about 76% of the total interactions, but in water they amount only to 2.6% (compare with the values in Table 8.1). Electron transfers between molecules are considered to occur in the condensed environment and only when such transfers are possible the interactions of the new type appear to replace the interactions of the polar part.

Namely, Gutmann's donor-acceptor approach seems to work better than the polar view point (Gutmann, 1978; Mittal and Anderson, 1991).

If only the dispersion forces are responsible for the intermolecular forces, the work of cohesion, Eq. 8.1, is the free energy change in dividing a material into two separate free flat surfaces from an initial intermolecular distance of r_1 to an infinity. From Exercise 8.1,

$$W_{11}^{\text{coh,d}} = 2\gamma_1^{\text{d}} = -\Delta G_{11}^{\text{d}} = \frac{A_{11}}{12\pi r_1^2} \quad (8.6)$$

Similarly, if the force between two materials, 1 and 2, is only the dispersion force, the work of separating the two phases is given by

$$W_{12}^{\text{adh,d}} = -\Delta G_{12}^{\text{d}} = \frac{A_{12}}{12\pi r_{12}^2} \quad (8.7)$$

where r_{12} is the intermolecular distance.

A quantum-mechanical expression for the constant, β_{12} , of the dispersion energy can be approximated as (Exercise 8.3)

$$\beta_{12} = \frac{3\hbar}{2(4\pi\epsilon_0)^2} \frac{\omega_1\omega_2}{\omega_1 + \omega_2} \alpha_1\alpha_2 \simeq \frac{3\hbar}{2(4\pi\epsilon_0)^2} \left(\frac{\omega_1}{2} \frac{\omega_2}{2}\right)^{1/2} \alpha_1\alpha_2 \quad (8.8)$$

where the last two expressions are nearly equal if $\omega_1 \approx \omega_2$. Here, $\hbar\omega_1$ and $\hbar\omega_2$ are the first excitation energies of the interacting molecules, 1 and 2, respectively, and α_1 and α_2 are their polarizabilities. The Hamaker constant contains therefore the product of $\rho\alpha\omega^{1/2}$, which is associated with one of the two interacting particles (Exercise 8.9).

As Eq. 8.8 suggests and as we see in general, the interaction energies are proportional to the product of some molecular properties of interacting molecules. This approximation, called Berthelot's principle (London, 1937), has been sometimes used for an estimation of mixed Lennard-Jones parameters and second virial coefficients of gases. The intermolecular interactions will behave in the similar way. We may write

$$\begin{aligned} W_{AA} &= -A^2, \quad \text{and} \quad W_{BB} = -B^2 \quad (\text{for like molecules}) \\ W_{AB} &= -AB = -(W_{AA}W_{BB})^{1/2} \quad (\text{for unlike molecules}) \end{aligned} \quad (8.9)$$

Therefore, we approximate r_{12} and A_{12} of Eq. 8.4 by the geometric means:

$$r_{12} = (r_1 r_2)^{1/2}, \quad \text{and} \quad A_{12} = (A_{11} A_{22})^{1/2} \quad (8.10)$$

Then,

$$W_{12}^{\text{d}} = (A_{11} A_{22})^{1/2} / (12\pi r_1 r_2)$$

and from Eq. 8.6 we have

$$W_{12}^d = 2(\gamma_1^d \gamma_2^d)^{1/2} \quad (8.11a)$$

This is an important empirical relation to find the work of adhesion from the values of surface tensions if the dispersion forces are predominant in the intermolecular interactions. We can also use this relation if we know the part of the dispersion contribution to the surface tension, like in the case of hydrocarbon chains and water. (See an exception related with Eq. 11.23 and others in Israelachvili, 1991, p. 142.) In addition, by substituting Eq. 8.11a into Eq. 8.1 we have

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} \quad (8.11b)$$

When a medium, 3, is intervening between the particles, 1 and 2, the Hamaker constant is approximated by (see Eq. 8.47)

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (8.12)$$

If two equal spheres of material 1 are interacting separated by a thin film of material 3 (Exercise 8.10),

$$\Delta G_{131}^d = -(A_{11} + A_{33} - 2A_{13})a/12H \quad (8.13)$$

where H is the shortest distance between the surfaces of the spheres.

The work of adhesion in a third medium, 3, is given by

$$W_{132}^{\text{adh}} \text{ in medium 3} = \gamma_{13} + \gamma_{23} - \gamma_{12} \quad (8.14)$$

The above approach to the dispersion forces starts from the atomic structure of particles. There is another approach of Lifshitz (1956), where the atomic structure is ignored and the forces between large bodies are driven in terms of their bulk properties, such as their dielectric constants. Of course, the only difference between the approaches lies in the way of calculating the Hamaker constant. However, the results of these two different approaches often turn out to be numerically very different and Lifshitz' theory seems to be better in practical cases. One reason for this is that Lifshitz' theory gives the way of handling the effect of the surrounding medium on the interacting bodies.

In addition, London's theory is essentially an electrostatic theory and for the zero absolute temperature. In fact, Eq. 8.8 refers to the case when all the molecules involved are in the lowest possible energy states. As the temperature is higher, the interactions among atoms and molecules cause their excitation and deexcitation and the emission and absorption of electromagnetic waves occur, the analysis being subject to statistical mechanics. The fluctuating electromagnetic fields are responsible for the van der Waals interaction and β_{12} becomes a func-

tion of temperature. We can consider the fluctuating electromagnetic fields as due to a collection of simple harmonic oscillations of some characteristic frequencies, like those frequencies emitted or absorbed by the molecules, of the system.

A simple illustration may be given by assuming that two macroscopic bodies, 1 and 2, consist of atoms, which can be modeled by two-level systems or simple harmonic oscillators. First we consider, for simplicity, the dipole-dipole interactions among oscillators without specifying the distribution of the oscillators separately between the two bodies. If the i -th oscillator or mode has a classical frequency of ω_i^0 when isolated, the Hamiltonian of the system can be written as

$$H = \frac{m}{2} \sum_i \left[\left(\frac{d\mathbf{x}_i}{dt} \right)^2 + (\omega_i^0)^2 \mathbf{x}_i^2 \right] - \frac{e^2}{2} \sum_i \sum_j \mathbf{x}_i \cdot \vec{\mathbf{F}}_{ij} \cdot \mathbf{x}_j \quad (8.15)$$

where m , e , and \mathbf{x}_i are the mass, charge, and displacement of the i -th oscillator at position \mathbf{r}_i , respectively. $\vec{\mathbf{F}}_{ij}$ is the tensor giving the field at \mathbf{r}_i due to an electric dipole (moment: $e\mathbf{x}_j$) at \mathbf{r}_j :

$$\begin{aligned} \vec{\mathbf{F}}_{ij} &= 0 \quad \text{if } i = j, \\ &= -\frac{1}{4\pi\epsilon_0} \nabla_i \nabla_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{if } i \neq j \end{aligned} \quad (8.16)$$

(For simplicity, we consider, for the time being, without the distinction between bodies, 1 and 2.)

The displacement vector \mathbf{x}_i of the i -th oscillator has three components. Therefore, we have altogether $3N$ independent components for N oscillators. We may relabel the components ($x_1, y_1, z_1, x_2, y_2, z_2, \dots \rightarrow 1, 2, 3, 4, 5, 6, \dots$), but proceed without changing the notations in the following.

In Eq. 8.15, assume the solution of the form, $\mathbf{x}_i = \mathbf{x}_i^0 \exp(-i\omega t)$ ($i=1,2,\dots,N$) and substitute it to Eq. 8.15. Then we obtain the secular equation for ω :

$$D(\omega) \equiv \left| [(\omega_i^0)^2 - \omega^2] \vec{\mathbf{I}} \delta_{ij} - \frac{e^2}{m} \vec{\mathbf{F}}_{ij} \right| = 0 \quad (8.17)$$

where the dimension of the determinant is $3N \times 3N$, giving $3N$ characteristic frequencies (normal modes). The dyadic $\vec{\mathbf{I}}$ is the 3×3 unit matrix and together with δ_{ij} ($i, j=1,2,\dots,N$) it makes a $3N \times 3N$ unit matrix. The mathematical procedure to handle the equation is the same as in the treatment of lattice vibrations in a solid. In the absence of the interaction the secular equation is

$$D_0(\omega) = |\{(\omega_i^0)^2 - \omega^2\} \vec{\mathbf{I}} \delta_{ij}| = \prod_i \{(\omega_i^0)^2 - \omega^2\} = 0 \quad (8.18)$$

The change of the zero-point energy of the oscillator system is given by the change of characteristic frequencies:

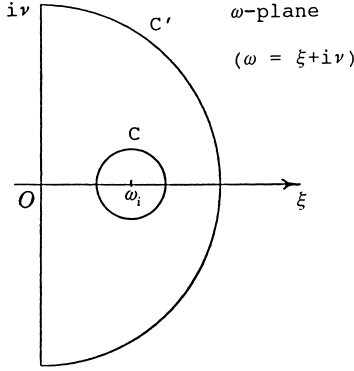


Fig. 8.1 Contours of the integrations for evaluating the zero point energy.

$$\begin{aligned}\Delta W &= (\hbar/2) \sum (\omega_i - \omega_i^0) \\ &= (\hbar/2) \sum [\{\text{Roots of } D(\omega) - \text{Roots of } D_0(\omega)\}] \end{aligned}$$

The secular equation, Eq. 8.17, can be written by diagonalizing as $D(\omega) = \prod_i (\omega_i^2 - \omega^2)$, where ω_i 's are the roots of $D(\omega)$. $D_0(\omega)$ has a similar expression with roots, ω_i^0 . The roots are real positive, but consider the complex- ω plane ($\omega = \eta + i\nu$; η, ν : real). We can then write ω_i (one of the roots of $D(\omega)$) in terms of a contour integral with the contour C or, equivalently, C' , in Fig. 8.1, around the root in the complex ω -plane (Arfken, 1970), as

$$\omega_i = \frac{1}{2\pi i} \oint \frac{\omega}{\omega_i - \omega} d\omega = \frac{1}{2\pi i} \oint \frac{2\omega^2}{\omega_i^2 - \omega^2} d\omega$$

This may be rewritten as

$$\omega_i = -\frac{1}{2\pi i} \oint \omega \left(\frac{d}{d\omega} \right) \ln(\omega_i^2 - \omega^2) d\omega \quad (8.19)$$

Since $\Delta W = (\hbar/2) \sum_i (\omega_i - \omega_i^0)$, using the contour C' , which is large enough to enclose all of the roots, which are finite, we can write

$$\Delta W = -\frac{1}{2\pi i} \oint \frac{\hbar\omega}{2} \frac{d}{d\omega} \ln \frac{D(\omega)}{D_0(\omega)} d\omega \quad (8.20)$$

$$= -\frac{\hbar}{4\pi i} \oint \ln \left| \overleftrightarrow{\mathbf{T}} \delta_{ij} - \frac{e^2}{m(\omega_i^{02} - \omega^2)} \overleftrightarrow{\mathbf{F}}_{ij} \right| d\omega \quad (8.21)$$

Equation 8.21 is obtained from Eq. 8.20 by integration by parts. Here, the bars inside the logarithm imply the determinant. On the large semi-circle of the contour

C' , where the real part of ω is very large, the second term, $e^2 \vec{F}_{ij}/m[(\omega_i^0)^2 - \omega^2]$, in the determinant of the integrand vanishes. Therefore, the integrand is simply $\ln |\vec{T}| = \ln 1$ and vanishes on the semi-circle. The remaining integration is carried out along the imaginary axis, where $\omega = i\nu$, so that we have

$$\Delta W = \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} \ln \left| \vec{T} \delta_{ij} - \frac{e^2}{m(\omega_i^{02} + \nu^2)} \vec{F}_{ij} \right| d\nu \quad (8.22)$$

Now, we use the identity: in the usual notation of matrices,

$$\ln |\mathbf{I} - \mathbf{A}| = \ln |\mathbf{I} - \mathbf{A}'| = \sum_i \ln(1 - A'_{ii}) = - \sum_i \sum_{n=1}^{\infty} \frac{1}{n} (A'_{ii})^n$$

where \mathbf{A}' is the diagonalized matrix of \mathbf{A} , with the diagonal elements A'_{ii} . Hence,

$$\ln |\mathbf{I} - \mathbf{A}'| = - \sum_{n=1}^{\infty} \frac{1}{n} \text{Tr}(\mathbf{A}^n) \quad (8.23)$$

where Tr denotes the trace (the sum of the diagonal elements, $\text{Tr} \mathbf{A} = \text{Tr} \mathbf{A}'$). Note that

$$\text{Tr} \mathbf{A} = \sum_{i=1}^{\infty} A_{ii}, \quad \text{Tr} \mathbf{A}^2 = \sum_{i,j=1}^{\infty} A_{ij} A_{ji}, \quad \text{Tr} \mathbf{A}^3 = \sum_{i,j,k=1}^{\infty} A_{ij} A_{jk} A_{ki}, \quad \text{etc.}$$

where, for instance, A_{ij} is the ij element of the matrix \mathbf{A} . Note that \mathbf{A} corresponds to the second term in Eq. 8.22.

Therefore, in Eq. 8.22, if we denote by $\alpha_i(\omega)$ the atomic polarizability, $\varepsilon_0 e^2 / m[(\omega_i^0)^2 - \omega^2]$ (see Sec. 4.3), we have

$$\Delta W = - \frac{\hbar}{4\pi} \sum_{n=1}^{\infty} \frac{1}{n} \int_{-\infty}^{\infty} \text{Tr}(\alpha_i \vec{F}_{ij} / \varepsilon_0)^n \quad (8.24)$$

Note that $(\alpha_i \vec{F}_{ij} / \varepsilon_0)$ is the $3N \times 3N$ matrix and the diagonal elements of \vec{F}_{ij} vanish because of Eq. 8.16, but those of $(\alpha_i \vec{F}_{ij} / \varepsilon_0)^n$, in general, do not vanish if $n \neq 1$.

Since the oscillators are distributed between the two bodies without specifying, Eq. 8.24 does not specifically represent the interaction between the two bodies. (For the dependence of ΔW on the distance, see Mahanty and Ninham, 1976).

Now we can consider the interaction of two bodies as a function of the distance between them. The formalism required is again to find the secular equation, $D(\omega) = 0$. This equation determines normal modes of the system, which depend on the distance. The free energy of the system at T is then given by $-k_B T \sum_k Z_k$,

where Z_k is the partition function of the mode k ($Z_k = \sum_n \exp(-E_{k,n}/k_B T)$, $E_{k,n} = (n+1/2)\hbar\omega_k$), so that we find

$$\Delta G(T) = -k_B T \sum_{k=1}^{3N} \ln \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2}) \frac{\hbar\omega_k}{k_B T}} \quad (8.25)$$

$$= -k_B T \sum_k \left(-\frac{\hbar\omega_k}{2k_B T} + \sum_{n=1}^{\infty} \frac{1}{n} e^{-\frac{\hbar\omega_k}{k_B T} n} \right) \quad (8.26)$$

where ω_k 's are the roots of the secular equation. The form of $D(\omega)$ will be given later. Following the same procedure as shown in Eqs. 8.19 and 8.20, we have

$$\Delta G(T) = \frac{k_B T}{2\pi i} \oint d\omega \left(-\frac{\hbar\omega}{2k_B T} + \sum_{n=1}^{\infty} \frac{1}{n} e^{-\frac{\hbar\omega}{k_B T} n} \right) \frac{d}{d\omega} \ln D(\omega) \quad (8.27)$$

$$= -\frac{\hbar}{2\pi i} \oint d\omega \left(\frac{1}{2} + \sum_{n=1}^{\infty} e^{-\frac{\hbar\omega}{k_B T} n} \right) \ln D(\omega) \quad (8.28)$$

The last equation is obtained by integration by parts. We will see later that $D(\omega) \rightarrow 1$ as $\omega \rightarrow \infty$. Therefore, as before, Eq. 8.28 can be changed to an integral along the imaginary axis.

$$\Delta G(T) = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} dv \left(\frac{1}{2} + \sum_{n=1}^{\infty} e^{-i \frac{\hbar v}{k_B T} n} \right) \ln D(iv) \quad (8.29)$$

Noting that $e^{-inx} = \cos(nx) - i\sin(nx)$, if we separate the exponential parts of Eq. 8.29 to cosine and sine terms, we find that the integral of the sine parts vanish since they are anti-symmetric about $v=0$. In order to simplify further, we use the identity:

$$\sum_{n=1}^{\infty} \cos(nx) = \pi \sum_{-\infty}^{\infty} \delta(x - 2\pi n) - \frac{1}{2}$$

If the order of the summation and the integral of Eq. 8.29 is interchanged, we have, indicating by Σ' that the $n=0$ term is to be divided by 2,

$$\Delta G(T) = k_B T \sum_{n=0}^{\infty}{}' \ln D(iv_n), \quad v_n = \frac{2\pi k_B T}{\hbar} n \quad (8.30)$$

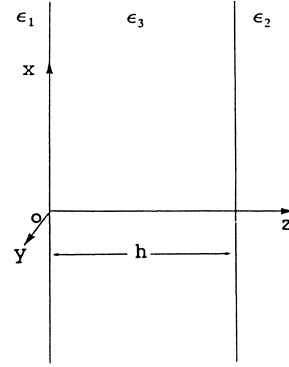


Fig. 8.2 The two-slab problem.

If the calculation includes the distance between two bodies, the force acting between the two is given by $-V(\Delta G(T))$.

Now we consider the way of introducing the distance between the two bodies into $D(\omega)$. We use an explicit example for illustration when there is an intervening media between two macroscopic bodies. As shown in Fig. 8.2, two semi-infinite slabs of dielectric constant, ϵ_1 and ϵ_2 , are interacting across a third medium, ϵ_3 , between them. Choose the coordinates as shown. For simplicity, we assume an electrostatic case, so that the electrostatic potential, $\phi(x, y, z)$, satisfy the Poisson equation:

$$\nabla^2 \phi(x, y, z) = 0 \quad (8.31)$$

Assuming that $\phi(x, y, z) = \phi(x)\phi(y)\phi(z)$ and that $\phi(x)$ and $\phi(y)$ behave in the same way in the three media (there is a translational symmetry in the x and y directions), $\phi(x)\phi(y) = \text{some constant} \cdot \exp[\pm i(k_x x + k_y y)]$, k_x and k_y being real, the Poisson equation leads to

$$\frac{d^2 \phi(z)}{dz^2} - k^2 \phi(z) = 0 \quad (8.32)$$

where $\mathbf{k} = (k_x, k_y)$ and $k^2 = k_x^2 + k_y^2$, being the same value for the three media because of the geometrical symmetry. The solutions are given by

$$\begin{aligned} \phi(z) &= A \cdot \exp(kz), & z < 0 \\ &B \cdot \exp(kz) + C \cdot \exp(-kz), & 0 < z < h \\ &D \cdot \exp(-kz) & z > h \end{aligned} \quad (8.33)$$

with $k \geq 0$. We have chosen these solutions, so that they do not diverge at $z = \pm \infty$. These solutions must be connected by the boundary conditions, such that ϕ and $-\epsilon_0 \epsilon_{1,2, \text{ or } 3} (d\phi/dz)$ must be continuous at $z=0$ and h .

$$\begin{aligned} \text{At } z = 0, \quad A &= B + C, \\ \varepsilon_1 k A &= \varepsilon_3 k B - \varepsilon_3 k C \end{aligned}$$

Therefore,

$$(\varepsilon_1 - \varepsilon_3)B + (\varepsilon_1 + \varepsilon_3)C = 0$$

We have similar relation at $z=h$, i.e., $(\varepsilon_2 + \varepsilon_3)B + (\varepsilon_2 - \varepsilon_3)e^{-2kh}C = 0$. Eliminating A , B , and C , we have the secular equation,

$$\begin{vmatrix} \varepsilon_1 - \varepsilon_3 & \varepsilon_1 + \varepsilon_3 \\ \varepsilon_2 + \varepsilon_3 & (\varepsilon_2 - \varepsilon_3)e^{-2kh} \end{vmatrix} = 0 \quad (8.34)$$

Now, we assume that Eq. 8.34 holds for an oscillating case with frequency ω , so that ε 's are functions of ω . We rewrite Eq. 8.34 as

$$D(\omega; 2kh) \equiv 1 - \Delta_{13}\Delta_{23} \exp(-2kh) = 0 \quad (8.35)$$

where $\varepsilon(\omega)$'s behave as shown by Eq. 4.95 and

$$\Delta_{i3}(\omega) = \frac{\varepsilon_i(\omega) - \varepsilon_3(\omega)}{\varepsilon_i(\omega) + \varepsilon_3(\omega)}, \quad i = 1, 2 \quad (8.36)$$

Note that the space is extending uniformly in the x and y directions, so that k_x and k_y are continuous. The interaction energy is then given by summing the zero-point energy per unit area, including all the possible values of k and subtracting the energy for $h \rightarrow \infty$ (see Eq. 8.20 and Exercise 8.16). Note that the summation over k_x and k_y per unit area can be here replaced by $\int \int dk_x dk_y / (2\pi)^2$ as explained by Jackson (1975, p. 68).

A more general method for the potential problem, Eq. 8.31, is to use the Green function. For the above electrostatic problem, it is the solution of the Poisson equation with a charge of a unit strength at position \mathbf{r}' .

$$\nabla^2 G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (8.37)$$

with boundary conditions that G and $\varepsilon(dG/dz)$ are continuous at $z=0$ and h . Ma-hanty and Ninham (1976, p. 215) has given the solution, which gives the same secular equation as Eq. 8.35. If retardation must be included, the retarded Green function satisfying the time-dependent equation:

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) G(\mathbf{r}, t; \mathbf{r}', t') = -\delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (8.38)$$

or the solution of the full Maxwell equations may be used (Mahanty and Ninham, 1976, p. 38 and p. 100; Gregory, 1981).

We can find the temperature dependence of the interaction energy for the two-half-space system. Following the procedures used to obtain Eq. 8.28 and noting that the summations on k_x and k_y can be replaced by integration as described before, we obtain the Gibbs free energy per unit area of the system (no retardation).

$$\Delta G(T) = -\frac{\hbar}{2\pi i} \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \int_{-\infty}^{\infty} \frac{dk_y}{2\pi} \oint d\omega \left(\frac{1}{2} + \sum_{n=1}^{\infty} e^{-\frac{\hbar\omega}{k_B T} n} \right) \ln D(\omega; 2kh) \quad (8.39)$$

Defining $x \equiv 2kh$, we find that $dk_x dk_y \rightarrow k dk d\phi \rightarrow (1/4h^2) x dx d\phi$, where ϕ is the azimuthal angle. Since $\int d\phi \dots = 2\pi \dots$, we can write

$$\Delta G(T) = \frac{\hbar}{16\pi^2 h^2} \int_0^{\infty} x dx \int_{-\infty}^{\infty} dv \left(\frac{1}{2} + \sum_{n=1}^{\infty} e^{-i \frac{\hbar v}{k_B T} n} \right) \ln D(iv; x) \quad (8.40)$$

$$= \frac{k_B T}{8\pi h^2} \int_0^{\infty} x dx \sum_{n=0}^{\infty} \ln D(iv_n; x), \quad v_n = \frac{2\pi k_B T}{\hbar} n \quad (8.41)$$

Here, Eq. 8.30 is used to obtain Eq. 8.41. When $\epsilon_3 = 1$ (vacuum), $\Delta G = -A_{12}/12\pi h^2$ (Exercise 8.1). Finally, the Hamaker constant is given by

$$A_{132} = -\frac{3k_B T}{2} \int_0^{\infty} x dx \sum_{n=0}^{\infty} \ln(1 - A_{13}(iv_n) A_{23}(iv_n) e^{-x}) \quad (8.42)$$

$$= \frac{3k_B T}{2} \sum_{n=0}^{\infty} \int_0^{\infty} x dx \sum_{m=1}^{\infty} \frac{1}{m} (A_{13} A_{23} e^{-x})^m \quad (8.43)$$

$$= \frac{3k_B T}{2} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{1}{m^3} (A_{13}(iv_n) A_{23}(iv_n))^m \quad (8.44)$$

If the difference of dielectric constants, $\epsilon_i - \epsilon_3$ ($i=1,2$), is small, only the term $m=1$ in the summation over m is important and we have a usual expression:

$$A_{132} = \frac{3k_B T}{2} \sum_{n=0}^{\infty} \frac{\varepsilon_1(iv_n) - \varepsilon_3(iv_n)}{\varepsilon_1(iv_n) + \varepsilon_3(iv_n)} \cdot \frac{\varepsilon_2(iv_n) - \varepsilon_3(iv_n)}{\varepsilon_2(iv_n) + \varepsilon_3(iv_n)}, \quad v_n = \frac{2\pi k_B T}{\hbar} n \quad (8.45)$$

Note that $v_n \sim 2.5 \cdot 10^{14} n \text{ s}^{-1}$ at 300 K. Here, the $n=0$ term corresponds to the zero-frequency energy of the van der Waals interaction and includes low-frequency Debye dipolar contributions. The remaining terms give the dispersion energy and include the London energy contribution of Eq. 8.4. The density dependence of Eq. 8.19 through $\varepsilon(iv_n)$ is much more complicated than Eq. 8.4. In particular, Eq. 8.17 or 8.19 automatically contains the bathing medium 3. From Eq. 4.95, we can approximately write

$$\varepsilon_0 \varepsilon_j(iv) = \varepsilon_0 + \rho_j \alpha_j(iv), \quad j = 1, 2, 3 \quad (8.46)$$

Replacing $\sum_n \rightarrow (\hbar/2\pi k_B T) \int dv$, we can write, diving the $n=0$ term by 2 in Σ' ,

$$A_{132} = \left(\frac{3k_B T}{16\varepsilon_0^2} (\rho_1 \alpha_1(0) - \rho_3 \alpha_3(0)) [\rho_2 \alpha_2(0) - \rho_3 \alpha_3(0)] \right. \\ \left. + \frac{3\hbar}{16\pi\varepsilon_0^2} \int_{v_1}^{\infty} [\rho_1 \alpha_1(iv) - \rho_3 \alpha_3(iv)] [\rho_2 \alpha_2(iv) - \rho_3 \alpha_3(iv)] dv \right) \quad (8.47)$$

By expanding Eq. 8.47 and noting Eq. 8.4, we obtain Eq. 8.12.

In Eq. 8.47, if the medium 3 is vacuum, $\alpha_3=0$ and we have

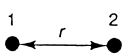
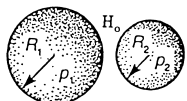
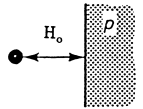
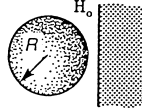
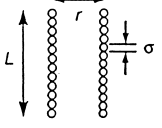
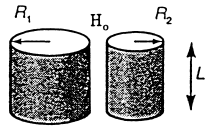
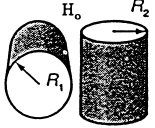
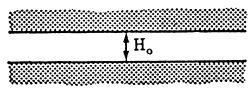
$$A_{12} = \rho_1 \rho_2 \left[\frac{3k_B T}{16\varepsilon_0^2} \alpha_1(0) \alpha_2(0) + \frac{3\hbar}{16\pi\varepsilon_0^2} \int_{v_1}^{\infty} \alpha_1(iv) \alpha_2(iv) dv \right] \quad (8.48)$$

At $T=0$, the integral part must be associated with the zero-point energy of the system, corresponding to the specific configuration. If the configuration changes, the zero-point energy also changes.

The Gibbs free energies for various geometries are listed in Table 8.2.

From Eq. 8.47, some Hamaker constant is expected to be negative, corresponding to a repulsive case. This happens, for instance, for a water-hydrocarbon-air system, a fused quartz-water-air system, etc. In some cases, the static term, the first term of Eq. 8.47, could be negative but small, but the second term is positive and larger, so that the total Hamaker constant can be positive at a certain short distance of separation. But at a larger distance the retardation effect will be important and reduce the value of the second term and the total Hamaker constant becomes negative, i.e. repulsive.

Table 8.2 Non-retarded Gibbs free energies for various geometries (C : β_{12} , Eq. 8.3; p : density; A : Hamaker constant; Israelachvili, 1991, with permission from Academic Press)

<p>Two atoms</p>  <p>$\Delta G = -C/r^6$</p>	<p>Two spheres</p>  <p>$\Delta G = \frac{-A}{6H_0} \frac{R_1 R_2}{(R_1 + R_2)}$</p>
<p>Atom-surface</p>  <p>$\Delta G = -\pi C p / 6 H_0^3$</p>	<p>Sphere-surface</p>  <p>$\Delta G = -A R / 6 H_0$</p>
<p>Two parallel chain molecules</p>  <p>$\Delta G = -3\pi C L / 8 \sigma^2 r^5$</p>	<p>Two cylinders</p>  <p>$\Delta G = \frac{A L}{12\sqrt{2} H_0^{3/2}} \left(\frac{R_1 R_2}{R_1 + R_2} \right)^{1/2}$</p>
<p>Two crossed cylinders</p>  <p>$\Delta G = -A \sqrt{R_1 R_2} / 6 H_0$</p>	<p>Two surfaces</p>  <p>$\Delta G = -A / 12\pi H_0^2$ per unit area</p>

Van Oss et al. (1980) found that whenever the Hamaker constant for polymer-solvent-air systems exceeds about $0.03 \cdot 10^{-13}$ erg the polymers are miscible with each other in the solvent, while the constant $< -0.03 \cdot 10^{-13}$ erg they are immiscible and phase separation occurs. This behavior, however, depends on the concentrations.

When two surfaces or particles approach closer than a few nanometers, continuum theories of attractive van der Waals' forces often fail to describe their interactions. At small separations, the detailed molecular arrangement and additional forces will come into play. The additional forces can be monotonically repulsive, or monotonically attractive, or oscillatory and they can be much stronger than the dispersion forces. The structure of solvent molecules at an interface has been reviewed by

Nicholson and Parsonage (1982), Ciccotti et al. (1987), and Evans and Parry (1990). Computer simulations indicate that while the liquid density oscillations are not expected at a liquid-vapor or liquid-liquid interface, a very different situation arises at a solid-liquid interface, where liquid molecules at the interface appear in quasi-discrete layers extending several molecular diameters into the liquid. Liquids intervening two solid surfaces behave in the same way, and the liquid density oscillates with the distance of the two surfaces (Israelachvili, 1991, Chapt. 13).

8.1.3 Effects of Electrolytes on Dispersion Forces

One of the most important applications of the theory of van der Waals' forces in disperse systems is to the interaction of two materials separated by an aqueous electrolyte solution.

When two half-spaces are separated by an ionic solution, the dielectric properties of the solution are altered. The ions respond to low frequencies but not to higher frequencies given by ν_n ($n \neq 0$). In fact, since ions are free to move in the solution, they are not bound and the dielectric constant is given by

$$\varepsilon(\omega) = \varepsilon_s(\omega) - \frac{\omega_p}{\omega^2}, \quad \omega_p = \frac{q^2 N}{M}$$

where ε_s is the dielectric constant of the solvent and q and M are the charge and the mass of the ion, respectively, with the number density, N . The frequency, ω_p , is called the ion plasma frequency. For usual concentration of ionic solutions of 0.1 molar, $\omega_p \sim 10^{12} \text{ s}^{-1}$. If ω is $i\nu_1 = i2\pi k_B T/\hbar = i2.5 \cdot 10^{14} \text{ s}^{-1}$ or higher, ions do not contribute to the dielectric constant. But for low frequencies, the presence of ions becomes very important and substantially modify the response of the solution to an external field at zero frequency, because ions are redistributed by the force due to the field and screening will occur.

Richmond (1975) gave a linearized theory on the Hamaker constant for the interacting uncharged surfaces of half-infinite materials, intervened by an electrolyte, is given by (Exercise 8.18)

$$A_{131} = -\frac{3k_B T}{4} \int_0^\infty k dk \ln \left[1 - \left(\frac{\varepsilon_1 k - \varepsilon_3 s}{\varepsilon_1 k + \varepsilon_3 s} \right)^2 e^{-2sh} \right], \quad s^2 = k^2 + \kappa^2 \quad (8.49)$$

where h is the distance between the two surfaces, $k = (k_x^2 + k_y^2)^{1/2}$, and κ is the Debye-Hückel parameter,

$$\kappa = \left(\frac{e^2 \sum_i N_i z_i^2}{\varepsilon_0 \varepsilon k_B T} \right)^{1/2} \quad (8.50)$$

where N_i and z_i are the number density and the valency of the i -th ion, respectively. For $\kappa h \ll 1$, the ions have no effect, but for $\kappa h \gg 1$,

$$A_{131} \rightarrow -\frac{k_B T}{8\pi h} e^{-2\kappa h}$$

If the ionic strength or κ is large, the attraction decreases.

The more realistic problem occurs when two interacting surfaces are charged. It does not have a good theory, although the DLVO theory seems to be successful in treating the stability of charged particles (see Chapt. 11).

8.2 Numerical Evaluations of Lifshitz' Theory and Experiments on Dispersion Forces

8.2.1 Numerical Evaluations of $\varepsilon(i\nu)$

The values needed in Eq. 8.44 are the dielectric constants as a function of imaginary frequencies. Although the general expression of $\varepsilon(\omega)$ is given by Eq. 4.95, it is almost impossible to theoretically calculate the dielectric constants. However, Eq. 4.95 suggests an approximate method of experimentally determining the values from the absorption spectra of the material.

According to the Kramers-Kronig relation (Jackson, 1975), the real part of $\varepsilon(\omega)$ is given by

$$\Re \varepsilon(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \Im \varepsilon(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (8.51)$$

where P implies Cauchy's principal part and the \Im stands for the imaginary part, which is related to the absorption spectrum. We assume that $\varepsilon(i\nu)$ of Eq. 8.44 can be obtained from $\Re \varepsilon(\omega)$ by replacing ω by $i\nu$.

In Eq. 8.44, $\nu_n = n(2\pi k_B T / \hbar) \simeq 2.5 \cdot 10^{14} n \text{ s}^{-1}$ at 300 K, which is larger than the frequencies associated with molecular rotations (10^{12} s^{-1}). The dispersion energy terms for $n \neq 0$ are solely determined by the response of materials to optical frequencies. Suppose that a very narrow isolated absorption line or band occurs at $\omega = \omega_i$. If the absorption can be approximated by

$$\Im \varepsilon(\omega') \simeq \frac{\pi K_i \omega_i}{2} \delta(\omega' - \omega_i)$$

around frequency ω_i , where K_i is a constant associated with the strength of the absorption or the oscillator strength at ω_i . Substituting this into Eq. 8.51, we then have

$$\varepsilon(iv) \simeq \frac{K_i \omega_i^2}{\omega_i^2 + \nu^2} \quad (8.52)$$

near ω_i , omitting 1. Therefore, covering a large frequency domain ($i=1,2,\dots$), we can write

$$\varepsilon(iv_n) = 1 + \sum_i \frac{K_i}{1 + \nu_n(\nu_n + \gamma_i)/\omega_i^2} \quad (8.53)$$

where the damping constants, γ_i (Eq. 4.95), are included and

$$\varepsilon(0) = 1 + \sum_n K_i \quad (8.54)$$

This $\varepsilon(0)$ is the static dielectric constant.

Some material such as water contributes to the dielectric constant from the rotational relaxation frequencies of their dipoles in the microwave ($\sim 10^{11} \text{ s}^{-1}$) and infrared ($\sim 10^{14} \text{ s}^{-1}$) regions. In this case, we have to include terms

$$\sum_r \frac{K_r}{1 + \nu_n/\omega_r} \quad (8.55)$$

into Eq. 8.53.

For metals, free electrons are main contributors to the dielectric constant. Since they are not bound, their characteristic frequencies ω_k and the damping constants γ_k in Eq. 4.95 vanish to a good approximation. For higher frequencies $\omega (=iv_n)$, from Eq. 4.95 (with $f_k=1$) we have

$$\varepsilon(iv_n) = 1 + \frac{\omega_p^2}{\nu_n^2}, \quad \omega_p^2 = \frac{Ne^2}{m} \quad (8.56)$$

The frequency, ω_p , is called the plasma frequency, typically in the range of $(3-5) \cdot 10^{15} \text{ s}^{-1}$.

The absorption spectrum is usually complicated, but fortunately only a few well-isolated absorption lines or narrow bands are strong and important to contribute to the dielectric constants, Eqs. 8.53 and 8.55. This is because the masses of electrons (m) and molecules (M) are quite distinct. If a molecule is isolated, the ratio of the molecular vibrational frequencies, ω_{vib} , and electronic frequencies, ω_e , is of order of $(m/M)^{1/2}$ and that of the molecular rotational relaxation frequencies, ω_{rot} , and ω_e is around m/M , which is 10^{-3} – 10^{-5} . Only one absorption line or band has a large oscillator strength (f_k) and is important in each of these three frequency regions. If the molecule is in a solution, the absorption in ω_{rot} is due to the relaxation of a molecular permanent dipole. Under an external electric field, the dipole tries to orient in the direction of the field, but it will be in thermal

Table 8.3 Optical constants for water [$K_r=74.8$, $\omega_r=9.85 \cdot 10^{10} \text{ s}^{-1}$ in Eq. 8.55]

$\omega_i (\times 10^{16} \text{ s}^{-1})$	K_i	$\gamma_i (\times 10^{15} \text{ s}^{-1})$
$3.14 \cdot 10^{-3}$	9.61	$2.27 \cdot 10^{-2}$
$1.05 \cdot 10^{-2}$	4.81	$5.76 \cdot 10^{-2}$
$1.40 \cdot 10^{-2}$	0.99	$4.25 \cdot 10^{-2}$
$3.03 \cdot 10^{-2}$	0.94	$3.79 \cdot 10^{-2}$
$6.37 \cdot 10^{-2}$	0.51	$8.49 \cdot 10^{-2}$
1.25	0.260	0.773
1.52	0.372	1.33
1.73	0.608	2.34
1.97	1.03	3.11
2.26	1.00	4.49
2.80	1.80	9.49

Data from Parsegian (1975) are changed from eV to the above unit.

equilibrium with other dipoles and the orientation tries to be random, leading to the relaxation with the relaxation time τ_r , $1/\tau_r$ being of order of the rotational frequencies. In the electronic absorption, only the so-called resonant line, associated with an electronic allowed transition between the lowest electronic level and the next higher level, is strong. Therefore, a good approximation to the dielectric constants is given by

$$\varepsilon(i\nu_n) = 1 + \frac{\varepsilon(0) - K}{1 + \nu_n \tau_r} + \frac{K - n^2}{1 + (\nu_n/\omega_{\text{vib}})^2} + \frac{n^2 - 1}{1 + (\nu_n/\omega_e)^2} \quad (8.57)$$

where n is the refractive index at ω_e . Usually, ω_{rot} , ω_{vib} , and ω_e are in the microwave, the infrared, and the visible or ultraviolet regions, respectively. Therefore, a few experimental measurements are sufficient to numerically obtain a good approximation of $\varepsilon(i\nu_n)$.

Table 8.3 gives the constants for water to be used in Eq. 8.44.

8.2.2 Experiments on Van der Waals' Forces

Adhesion, physical adsorption, the strength of solid have been extensively studied by measuring the work necessary to separate two surfaces, or the centrifugal force necessary to separate a particle from a solid surface. But these involve short chemical bonds, which can strongly overshadow the desired results. The successful approach, first reported by Derjaguin et al. in 1954, is to measure the attractive force between carefully prepared surfaces as they are slowly brought together. Another method is to measure the disjunctive pressure in a liquid film as the film thins. But the distances were large, and the results agreed with Lifshitz theory for retarded interactions. However, Tabor and Winterton (1968) and Israelachvili and

Tabor (1972) measured with improved equipment (called Jacob's box) to enable to approach to 1.4 nm and their results confirmed Lifshitz nonretarded theory. Rabinovich et al. (1982) confirmed the theory with crossed glass fibers down to molecular distances.

Any quantity which depends on the dispersion forces can be used for the indirect measurements. For instance, if the surface tension is related only to the dispersion forces, the work of cohesion and adhesion can be used to obtain the Hamaker constant. Namely, from Eqs. 8.6 and 8.7 we have

$$A_{11} = 24\pi r_1^2 \gamma_1^d \quad \text{and} \quad A_{12} = 12\pi r_{12}^2 W_{12}^{\text{adh},d} \quad (8.58)$$

If the surface tension is known by some means, A_{11} can be determined. An interesting example is due to Croucher (1981), who used thermal expansion. If the molecular interaction is approximated by the potential $(6, \infty)$ in Eq. 3.31, then, with the coefficient, α , of the thermal expansion, the Hamaker constant is given by

$$A_{11} = \frac{3k_B T}{4 \left(1 - \frac{3+6\alpha T}{3+7\alpha T} \right)} \quad (8.59)$$

Marra (1986) has shown that retardation effects in liquids appear at smaller separations than in air (~ 5 nm rather than 10 nm).

Exercises

- 8.1** Use Eq. 8.3 and calculate the free energy, per unit area, between two planar parallel slabs of thicknesses, b_1 and b_2 , separated by a shortest distance h . The result must be

$$\Delta G_{12}^d = -\frac{A_{12}}{12\pi} \left[\frac{1}{h^2} - \frac{1}{(h+b_1+b_2)^2} - \frac{1}{(h+b_1)^2} - \frac{1}{(h+b_2)^2} \right]$$

For very large b_1 and b_2 (semi-infinite bodies)

$$\Delta G_{12}^d = -\frac{A_{12}}{12\pi h^2}$$

- 8.2** List examples of types of intermolecular interaction energies of two molecules. In particular, keep in your mind that the interaction energies are the product of some molecular properties of respective molecules.
- 8.3** Establish Eq. 8.8. For this purpose, consider, for simplicity, two hydrogen atoms, A and B, in the lowest energy states, 0. According to quantum-mechanics, the van der Waals interaction energy between the two atoms is given by

$$W_{AB}(r) = -\frac{3e^4\hbar}{2m_e^2(4\pi\epsilon_0)^2} \sum_{m,n \neq 0} \frac{f_{0m}^A f_{0n}^B}{\omega_{0m}^A \omega_{0n}^B (\omega_{0m}^A + \omega_{0n}^B)} \frac{1}{r^6}$$

where e and m_e are the electronic charge and mass, respectively, f_{0m} is the oscillator strength appearing as f_k in Eq. 4.95 and

$$\omega_{0m} = (E_m - E_0)/\hbar$$

E_m and E_0 are energies of the m -th excited state and the ground state, respectively. Fortunately, the oscillator strength is very small except for f_{01} . Otherwise, the above infinite series is hardly evaluated. Note that $f_{01} \simeq 1$. From Eqs. 4.89 and 4.95, find the polarizability for the electrostatic case ($\omega \simeq 0$) and establish Eq. 8.8.

8.4 Establish Eqs. 8.11a and 8.11b.

8.5 In Exercise 8.3, the interaction energy is predicted to be proportional to $1/[\omega_{01}^A \omega_{01}^B (\omega_{01}^A + \omega_{01}^B)]$. This expression has the following integral representation.

$$\frac{1}{\omega_{0m}^A \omega_{0n}^B (\omega_{0m}^A + \omega_{0n}^B)} = \frac{2}{\pi} \int_0^\infty \frac{dv}{((\omega_{0m}^A)^2 + v^2)[(\omega_{0n}^B)^2 + v^2]}$$

Thus, by using the first term of the polarizabilities obtained from Eq. 4.95 with the vanishing damping constant γ_{01} , we can write the van der Waals interaction energy as

$$W_{AB} = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty dv \alpha_A(iv) \alpha_B(iv) \frac{1}{r^6}$$

(Note that the last relation holds even when all the oscillator strengths are important if $\sum \int \approx \int \sum$).

8.6 Consider a polarizable particle of polarizability α in a medium of dielectric constant, ϵ . (Note that the polarizability is the excess polarizability (see Exercise 6.5)). If an uniform external electric field E is introduced, show that the electrostatic interaction energy is given by $-(1/2)\alpha E^2$.

8.7 Consider a semi-infinite material consisting of a polarizable molecule of polarizability α . The number density of the molecules is ρ . Another half of the space is filled with a material of a dielectric constant, ϵ , in which a charge q is present at a distance H from the plane surface of the semi-infinite material. First show that the electrostatic energy between the charge q and a single polarizable molecule. Then, by integrating over the molecules in the semi-infinite material, show that the total electrostatic energy is given by

$$W(D) = -\frac{\pi\rho\alpha}{2} \left(\frac{q}{4\pi\epsilon_0\epsilon} \right)^2 \frac{1}{H}$$

(Use the result of Exercise 8.6. Ignore the interactions among the polarized molecules in the semi-infinite material.)

8.8 Two half-spaces, bounded by a plane, are filled with materials of dielectrics of ϵ_1 and ϵ_2 , respectively. A point charge, q , is in ϵ_1 and in front of the boundary plane at a

distance of h . Show, by treating the system as a boundary value or an image problem, that the electrostatic energy is given by (Jackson, 1975, p. 147)

$$W(h) = -\frac{q^2}{(16\pi\epsilon_0\epsilon_1)h} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}$$

- 8.9** In Exercise 8.8, consider that the medium of ϵ_2 consists of molecules of polarizability, α_2 . If the number density is ρ_2 , the electrostatic energy can be obtained by the sum of individual interactions between the molecules and the charge, q . Comparing this result with the result of Exercise 8.8, show that

$$\rho_2\alpha_2 = 2\epsilon_0\epsilon_1(\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1)$$

- 8.10** Using Eq. 8.3, we can calculate the free energy of interacting two spheres of radii, a_1 and a_2 , with centers at a distance R apart to obtain

$$\Delta G_{12}^d = -\frac{A_{12}}{6} \left(\frac{2a_1a_2}{R^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{R^2 - (a_1 - a_2)^2} + \ln \frac{R^2 - (a_1 + a_2)^2}{R^2 - (a_1 - a_2)^2} \right)$$

If possible, establish this relation. Otherwise, let H denote the shortest distance between the surfaces of the spheres and $a_1 = a_2$. Then, show that

$$\begin{aligned} \text{if } H \ll a, \quad \Delta G_{12}^d &= -\frac{A_{12}a}{12H} \\ \text{if } H \gg a \quad \Delta G_{12}^d &= -\frac{16A_{12}a^6}{9H^6} \end{aligned}$$

- 8.11** Use Eq. 8.16 and find an explicit form of the last term of Eq. 8.15. Identify the physical origin of the interaction.
- 8.12** Find equation of motion standing for the Hamiltonian, Eq. 8.15. And then obtain the secular equation, Eq. 8.17.
- 8.13** The relation, Eq. 8.19, is obtained in terms of Cauchy's theorem. Also, try to find the same result by using the identity:

$$\frac{1}{\omega_k - \omega} = P \frac{1}{\omega_k - \omega} + \pi i \delta(\omega_k - \omega)$$

where P stands for the Cauchy's principal value.

- 8.14** Obtain Eq. 8.26 from Eq. 8.25.
- 8.15** Establish Eq. 8.30.
- 8.16** Find the interaction energy between two semi-infinite slabs by summing the zero-point energy for the system, whose secular equation or dispersion relation is given by Eq. 8.35.
- 8.17** Establish Eq. 8.39.
- 8.18** In Eq. 8.31, if the intervening medium is a weak electrolyte and a weak electric double layer is present, the equation must be replaced at least by Eq. 10.18. Then, show Eq. 8.49.
- 8.19** Establish Eq. 8.55 for dipole rotations. (Note: rotations are not bound, but if the rotational orientation is not in thermal equilibrium there is a relaxation process with relaxation time $\tau_r = 1/\omega_r$.)

- 8.20** Consider a molecule of mass M with bound electrons of mass m_e . Show that the ratio of the molecular vibrational frequencies and electronic frequencies is $(m_e/M)^{1/2}$. (Atomic outermost electrons are responsible for atomic emission of visible light of frequency ω_e and molecular binding. If the electrons are bound to the molecule by a force, the nuclei must be bound by an equal and opposite force. Taking this force (force constant: k) to be responsible for the molecular simple harmonic motion (vibrational), the classical frequency $\omega_v = (k/M)^{1/2}$. Electrons are bound by the force of the same magnitude, so that $\omega_e = (k/m)^{1/2}$. Therefore, $\omega_v/\omega_e = (m/M)^{1/2}$. Noting that the molecular size and the atomic size are comparable and denoted by a , the molecular moment of inertia is $Ma^2/2$ and the rotational energy is \hbar^2/Ma^2 , while the electronic energy is \hbar^2/ma^2 , so that $\omega_{\text{rotational}}/\omega_e = m/M$.)
- 8.21** Does the retardation effect occur in the dipole-dipole interaction? Can the retardation effect make the dispersion interaction repulsive at a certain separation (see Eq. 8.2)?

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